Microbial mediated arsenic biotransformation in wetlands

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Abstract

Arsenic (As) is a pervasive environmental toxin and carcinogenic metalloid. It ranks at the top of the US priority List of Hazardous Substances and causes worldwide human health problems. Wetlands, including natural and artificial ecosystems (i.e. paddy soils) are highly susceptible to As enrichment; acting not only as repositories for water but a host of other elemental/chemical moieties. While macro-scale processes (physical and geological) supply As to wetlands, it is the micro-scale biogeochemistry that regulates the fluxes of As and other trace elements from the semi-terrestrial to neighboring plant/aquatic/atmospheric compartments. Among these fine-scale events, microbial mediated As biotransformations contribute most to the element's changing forms, acting as the 'switch' in defining a wetland as either a source or sink of As. Much of our understanding of these important microbial catalyzed reactions follows relatively recent scientific discoveries. Here we document some of these key advances, with focuses on the implications that wetlands and their microbial mediated transformation pathways have on the global As cycle, the chemistries of microbial mediated As oxidation, reduction and methylation, and future research priorities areas.

Keywords

Arsenic, wetland, microbes, switch

1 Introduction

Arsenic (As) exists in four oxidation states (-III, 0, +III, and +V), and is present in both inorganic and organic forms. Commonly found in highly auriferous regions, As also associates with the mineral ores of other metals such as iron, copper, and lead [1]. Speciation in addition to concentration is fundamental to the understanding of As toxicity, mobility and fate in the environment [2]. In the biosphere, arsenate (As^{V}) and arsenite (As^{III}) are the most abundant inorganic As species. Under aerobic conditions, As^{V} dominates, is typically strongly absorbed to iron oxy-hydroxide minerals, and exhibits limited mobility/bioavailability [3]. Conversely, under anaerobis, a shift in As speciation to the trivalent form means the element is both more toxic and inherently more labile [3].

Common organic As species found in our bodies as well as in waters, soils, feeds and foods include monomethylarsenate ($MMAs^{V}$), dimethylarsenate ($DMAs^{V}$), trimethylarsine oxide (TMAsO), arsenosugars and arsenobetaine (AsB) (Table 1). They can be introduced into the environment due to microbial mediated biomethylation [4] and via anthropogenic activities, such as pesticide/fertilizer applications. Historically, the organic arsenical Roxarsone (2-nitrophenol-4-arsonic acid), has been added to poultry feeds as a growth promoter, however this has been largely phased out due to both animal and environmental health concerns [5]. Most, but not all, of the organic As species are considerably less toxic compared to their inorganic As counterparts. Typically, they are found **with** high concentrations in marine organisms. Arsenosugars constitute the main organo-As species found in algae, while in other marine dwellers, from lobsters to white fish, the toxin is packaged as the inert and very stable/unreactive AsB [6]. In freshwaters and soils/sediments, generally $MMAs^V$, $DMAs^V$ and volatile TMAsO are the most commonly detected organic As species [7].

As the interface between terrestrial and aquatic ecosystems, wetlands occupy between 5.3 and 12.8 million km^2 of the earth's surface [8]. Defined by their inundation by water and constant transition between wet and dry states, oxygen availability is typically very heterogeneous resulting in regions of water and sediment where anaerobism is commonplace [9]. Because of their wide distribution, high productivity, and rich biodiversity, wetlands have been viewed as having a major influence on many global biogeochemistries, including the carbon and nitrogen cycles [10, 11] in addition to impacting on As transfer [2].

Owing to their depositional characteristics, wetlands are also highly susceptible to contamination by heavy metals and other toxic trace elements. Macro-scale processes (physical and geological events), which include anthropogenic activities, wet, dry deposition, erosion, volcanism, and weathering are essential in determining As loading in these environments (Figure 1). Even seemingly 'pristine' wetland habitats/ecosystems, with Yellowstone National Park being a prime example [12], can be 'naturally' enriched in As. However, anthropogenic activities such as mining, smelting, urban waste and wastewater discharges, fertilizer and pesticide use also contribute significantly to the build-up of As stores in wetland [13]. Often, disconnected from the surrounding geology, these human induced redistributions of

As can be the hardest to predict and hence pose perhaps the greatest hazard to human health.

Despite the importance of macro-scale processes in determining As loading into wetlands, it is micro-scale biogeochemistry, which includes desorption, dissolution [14] and microbial mediated As^{V} reduction, As^{III} oxidation and methylation [2] that mainly regulate the fluxes of As from the semi-terrestrial to either aquatic or atmospheric compartments (Figure 1). Recent advances in molecular methods have enabled great leaps in our understanding of microbial mediated As biotransformations. This review summarizes the role of wetland microbiology within the global As cycle, and the distribution and behavior of As in water submerged soils and sediments. Moreover, it provides a detailed overview of the key transformation **biochemistries**, ranking the events in order of priority and discussing their interactions within a chemically complex and heterogeneous localized environment. Finally, an outlook for future research areas and introduction to emerging new technologies for measuring As cycling in wetlands is presented.

2 Distribution and behavior of As in wetlands

2.1 Overview

Wetlands can be broadly classified as either '*natural*', which includes marine, **coastal** zone and inland wetlands, or '*artificial*' wetlands such as paddy soils. Although, the true state of most systems is perhaps as a mixture/intermediary of the two. The definition of what constitutes, as a 'contaminated sediment' is similarly quite open to interpretation, as the acceptable quality criteria for As in wetland soils varies between countries (Table 2). For example, the Canadian Council of Ministers of the Environment (CCME), have set interim quality guidelines (ISQGs) for marine/estuarine sites at 7.24 mg kg^{-1} dry weight [15], whereas trigger thresholds in China are marked slightly higher, so a site is only given contamination status when concentrations of 20 mg kg^{-1} are breached [16]. An alternative method to evaluate the quality of a wetland, is to consider the As concentration in extractable waters. Recently reported incidences where detected As in overlying surface waters exceeded the US Environmental Protection Agency's (EPA) maximum containment level of As in drinking water (10 μg L^{-1}) are summarized in Table 3.

Perhaps the focal point of As contamination in wetlands, where to date most of the scientific research attention has been directed lies in southeast Asia [17-21]. Here the As source originally derived from eroded Himalayan rock, now resides as buried lens of sediment making up the Bay of Bengal Delta. These near-surface alluvia are the cause of As release to aquifers, and threaten tens of millions of people consuming these waters [22]. In samples collected from fifteen selected Bhaluka wetlands in Bangladesh, the concentration of As in the waters ranged from 7 to 80 μg L^{-1}, with 93% found exceeding WHO recommended permissible limits [23]. For further information on the Bangladesh As crisis, refer to reviews by Meharg *et al*. [24] and Meharg & Zhao [25].

Paddy field contamination in the region is also a serious problem, here high soil As concentrations are linked to the quality of the groundwaters used for irrigation [20].

This problem was uncovered in 2003, when seventy-one soils collected from three districts, revealed a range of As concentrations in soils spanning 3.1 mg kg^{-1} (*baseline*) up to 42.5 mg kg^{-1} [20]. While a later study by Stroud *et al*. [26], reported an even greater variation in total As concentrations in twelve paddy soils from Bangladesh, again similar baselines of 4 mg kg^{-1}, but this time the inputs of As from irrigation caused soils to reach 138 mg kg^{-1}. This highlights the ease in which As can accumulate in agricultural-wetland soils, which then leads to the direct transfer to food supply chains [20, 27].

China, meanwhile, is another country that has extensively studied the problem of As build-up in wetlands [28-31]. Here though the main inputs derive not from groundwaters, but instead take many different forms/guises. Although, often difficult to characterize due to the mixing of multiple and varying sources, they do share a commonality, in that inputs have intensified as the country had modernized. For example, freshwater and salt marsh sediments in **the** Yellow **river** delta, before the Xiaolangdi reservoir was built, were already As enriched, recording values of 30 mg kg^{-1}. However, after it was constructed, changes to the sediment flows coupled with increased human settlement and activity in the area, resulted in further As deposition taking the concentration up to 45 mg kg^{-1} [32], equivalent to a 4.5-fold increase from baseline levels for soils in the Yangtze river delta [33].

Like Bangladesh, paddy field contamination is also a topic of importance in China, with numerous studies highlighting this as a prominent issue, see Table 3 [28-31, 34]. However, total As concentrations only tell part of the story. Here As species are essential to understand the bioavailability and uptake of As in rice. Based on soil pore waters collected from Bangladesh and Chinese paddy soils, As^{III} is the dominant species, accounting for 66-100% of the total As [26]. Methylated As species ($DMAs^{V}$ and $MMAs^{V}$) are also commonly detected in rice soils [34]. Although the uptake of organic As into rice is not as rapid as As^{III}, once inside roots they quickly translocate to the above-ground tissues [25]. Volatile $TMAs^{III}$ has also been recently detected in field studies of paddy soils from Spain and Bangladesh, albeit only at trace-concentrations [35].

Far from just being confined to Asia, the problem of As contamination in **wetlands** is a feature on other continents as well. For example, concentrations of total As in twenty-five surface sediments (0-4 cm) collected from wetlands in Massachusetts in the U.S., ranged from 20 to 2100 mg kg^{-1} [36]. In southwest Spain, the contamination by As in the Guadalquivir marshes, arising from the mine-tailing spill in Aznalcollar, led to severe wetland soil pollution, with far reaching biological effects for local wildlife, a subject covered in depth by a number of related publications (Table 3) [37-39].

2.2 Biogeochemistry of As transformation and transport in wetlands

The predominant form of As in soil prior to flooding is As^{V}. Bound commonly to iron (oxy)hydroxides, due in equal measure to it's high affinity for the species and abundance in most soils, the labiality and subsequently toxicity of As^{V} is relatively low [40]. Saturating the system with water causes soil redox potentials to rapidly decrease, in response to the depletion of electron acceptors, such as oxygen, nitrate, manganese oxides and iron oxides/hydroxides. When Eh drops to below -200 mV porewater As^{V} concentrations decline as the species is transformed to As^{III} [25]. In the short-term, buffering can occur, because in these highly reducing conditions iron oxides/hydroxides are solubilized, releasing As^{V}. However, As^{III} development will dominate overtime [25, 41, 42]. This phenomenon can be further enhanced, by the direct reduction of soil reservoirs of As^{V}. Due to As^{III} being less strongly bound to soil particle surfaces than As^{V}, it partitions more readily into solution phase, increasing the overall bioavailability of the toxin [40, 43].

Organic carbon (OC) has also been shown to mobilize As in aquifers in south Bangladesh [44], while high concentrations of dissolved organic matter (DOM) in soil porewaters can complete with surface absorbed As^{V} and As^{III} displacing them into solution [21, 25]. Other important chemistries that control As transport, include the grouping of interactions that As has with sulfur rich minerals [45]. Under highly reducing conditions, and in the presence of dissolved sulfide, As^{III} can form stable complexes, for example, orpiment (As_2S_3) or realgar (As_4S_4) [36]. Immobilizing As by controlling redox conditions, to favor As-S precipitation, is a prac**tice** used in constructed **wetlands** for reducing As bioavailability [46]. However, the sites still require careful management, as oxidation of the sediment can result in the dissolution of sulfides and re-mobilization of As^{III} back into the environment [47, 48].

3 Mechanisms of microbial mediated As biotransformation in wetlands

Compared to chemical change, microbial mediated As redox reactions occur far more rapidly [49]. Study has showed As^{V} reduction in soils to be significantly suppresses when γ-irradiated, highlighting the dominant role the microbiota play in this in solum As transfer step [40]. Microbial activity can be increased/simulated by enhancing the availability of OC sources, a response that differs between species/communities. This in turn contributes to different rates and forms of As biotransformation, impacting on both inorganic and methylated As trends [28]. Indeed, most methylated As species detected in wetlands are originally derived from microbial mediated As reactions [31, 35], because plants are not efficient at methylating inorganic As [50]. These different As species with their ranging properties/characteristics define the manner that As is transferred back and forth from the main land and aquatic stores [51-54]. Some volatile As is released into the atmosphere, in the form of AsH_3, CH_3AsH_2 ($MeAsH_2$), $(CH_3)_2AsH$ (Me_2AsH), and $(CH_3)_3As$ ($TMAs^{III}$). However compared to the land and water exchanges the fluxes are relatively minor [28, 35].

The evolution of such effective and diverse microbial mediated As biotransformation systems arose because they protect against As toxicity. The pathways of how microbes deal with As have been extensively studied in the last couple of decades, revealing various genes and enzymes responsible for As biotransformation and its biotransportation out of cells [50, 55-57]. The main systems used in As biotransformation by microbes in wetlands are further summarized below.

3.1 As^{III} oxidation in wetlands

Rapid As^{III} oxidation in the environment is mediated by metabolic microbial processes [1, 58], which are catalyzed by As^{III} oxidase (Aio). This enzyme is encoded by *aioA* and *aioB* genes for the two subunits AioA (AoxB) and AioB (AoxA) [55, 59]. Microbial mediated As^{III} oxidation is considered as one of the primary As detoxification mechanisms for microbes because it can oxidize As^{III} to the less toxic As^{V} [55]. The high abundance of *aioA* genes in paddy soils under flooding conditions further suggests the importance of this pathway [31, 60]. As^{III} oxidizing bacteria in paddy soils mainly assign to the following family groupings: *Phyllobacteriaceae*, *Bradyrhizobiaceae*, *Methylobacteriaceae*, *Rhizobiales*, *Burkholderiales* and *Comamonadaceae* [60, 61].

In other types of wetland, for example coastal sediments, a high diversity of *aioA*-like genes have also been detected. The most abundant *aioA*-like genes derived from *Roseobacter litoralis* Och 149 [62]. As^{III} oxidizing bacteria isolated from natural and constructed wetlands in the Republic of Korea showed that they were all able to grow in the presence of high concentrations of As^{III} (10 mM). The bacterium identified as *Pseudomonas stutzeri* strain GIST-BDAN2 showed an especially high activity of As^{III} oxidation (completely oxidized 1 mM As^{III} to As^{V} within 25-30 h) and possessed both the *aoxB* and *aoxR* genes [63]. Three As^{III} oxidizing bacteria including *Agrobacterium tumefaciens, Pseudomonas fluorescens,* and *Variovorax paradoxus*-like organisms were also isolated from the same Madison River Valley soils that also supported large populations of As^{V} reducing bacteria [64]. This highlights the close overlay of the microbial catalyzed oxidation and reduction pathways, and how this dichotomy functions as the principal ‘switch’ which controls As fate in a specific site or zone within a site.

3.2 As^{V} reduction in wetlands

Microbial mediated As^{V} reduction segregates into two functional schemes, the respiratory and the detoxification pathway. The respiratory pathway is catalyzed by the As^{V} respiratory reductase (ArrA) complex, which consists of a large catalytic subunit (ArrA) and a small subunit (ArrB) [65-67]. It can mediate anaerobic dissimilatory As^{V} reduction and couple this with energy production [68-70]. A more universal system of As^{V} detoxification reduction, is catalyzed by the cytoplasmic As^{V} reductase (ArsC), which is present in both aerobic and anaerobic microbes [71]. The *arsC* gene occurs in the *ars* operons next to the *arsB* gene that functions as an As^{III} membrane pump in most bacteria [56], controlling cytoplasmic As^{V} reduction, and thereafter As^{III} efflux.

In wetland sediments, microbial mediated As^{V} reduction is considered to be a crucial mechanism controlling As^{V} mobilization [72], and contributing factor leading to As contamination of ground water, as has happened in south and southeast Asia [22, 73]. Due to the anaerobic conditions encountered in wetlands, dissimilatory As^{V} respiring bacteria are quite commonplace. The dissimilatory As^{V} reduction gene *arrA* has been detected in various wetlands, including paddy soils [60, 61], coastal sediments from south China [62], and estuarine sediments from Chesapeake Bay in the U.S. [74]. Zhang *et al*. [34] revealed that *arrA* sequences detected in paddy soils were analogous to those found in *Geobacter* species, which have been frequently found in As rich sediments before [72, 75]. Similarly, *Geobacter* are prominent in Japanese paddy soil [54]. Observations of *Geobacter* species OR-1 have revealed that in addition to As, ferrihydrite is also being used as an electron acceptor, thus catalyzing the dissolution of As from As^{V}-absorbed ferrihydrite, by promoting ferrous iron formation [54]. Moreover, As K-edge X-ray absorption near-edge structure analysis demonstrated the OR-1 can also reduce soil/solid bound As^{V} directly. In addition to *Geobacter*-related bacteria, other microbiota, such as *Shewanella* species, that utilize the coupling/uncoupling of iron and As reduction as a means of acquiring energy, are also capable of dissimilatory As^{V} reduction [76, 77].

Similar to *arrA*, *arsC* has also been frequently detected in paddy soils [60, 61] and coastal sediments [62]. The As^{V} reducing microbes with the most active detoxification pathways in paddy soils mostly belonged to typically rhizospheric bacteria groups, such as *Rhizobiales* and *Pseudomonadales* [61]. Study of pure culture bacteria from Madison River Valley soils revealed five isolates, *Agrobacterium tumefaciens*, *Flavobacterium* sp., *Microbacterium* sp. and two *Arthrobacter* sp.-like organisms capable of rapidly reducing As^{V} under aerobic conditions, with the later found to possess new putative *arsC* genes [64]. Seventeen As-resistant bacteria isolated from Mandovi and Zuari estuarine water systems revealed *arsA* (ATPase), *arsB* and *arsC* genes on their plasmid DNA. While, *arsC* genes were individually detected in thirteen bacterial isolates, including the genera's *Halomonas* and

Acinetobacter [78]. Using genome sequencing of *Bacillus* bacterium isolated from Andean wetlands in northern Chile, the *arsC* gene function was found as detoxification As^{V} reduction [79]. Together with the As^{V} respiring bacteria, these detoxification As^{V} reducing microbes catalyze the reduction of both the soil absorbed As^{V} and dissolved As^{V} in solution into As^{III}.

3.3 As^{III} methylation and volatilization in wetlands

Organic As is introduced primarily into the environment via the microbial catalyzed methylation of As^{III}. The As^{III} *S*-adenosylme-thionine methyltransferase (ArsM), which is responsible for As^{III} methylation has recently been found to be common to many different microbes [12, 80-82]. It is encoded by *arsM* genes, and **catalyzes** the generation of less toxic organic As species, such as $MMAs^{V}$, $DMAs^{V}$ and TMAO. The volatile As gas including $MeAsH_2$, Me_2AsH and $TMAs^{III}$ could also be generated during the biomethylation processes. To date, $TMAs^{III}$ is the most commonly detected volatile As species in the natural environment [28, 35] and under *in vitro* conditions during pure culture [81-83].

In microcosm experiments using As contaminated paddy soils, Huang *et al*. [28] and Jia *et al*. [29] found evidence of both microbial mediated As^{III} methylation and volatilization. Recently discovered universal primers for the amplification of *arsM* genes have uncovered *arsM* sequences as being widespread in numerous paddy soils [29, 61]. Continued investigation reveals these *arsM* sequences mainly derive from the phyla *Gemmatimonadales*, *Firmicutes*, *Actinobacteria*, and *Proteobacteria* and the domain *Archaea* [61]. By applying a metagenomic approach, Cai *et al*. [62] also found *arsM* genes in coastal sediments, but the dominant bacteria species involved in As^{III} methylation were not identified in this study. Furthermore the ability to methylate and volatilize As^{III} has been discovered in three cyanobacteria species that are common in paddy soils [82], and a small free-living eukaryote *Ostreococcus tauri* found in coastal waters [83]. In general, to the best of our knowledge, the study of As^{III} methylation and volatilization in wetlands is still rather limited, but given the rapid advance in our understanding of the importance of this aspect of the As biogeochemical cycle, this is an area that will likely be of increasing interest in the future.

3.4 Environmental factors affecting As biotransformation microbes

Various environmental factors affecting the diversity, behavior and metabolism of As biotransformation microbes have been observed in wetlands. One of the most important is the As concentration of the soils/sediments with As biotransformation microbe abundance found to correlate positively with As concentration in paddy soils [61]. Similarly, *arsM* gene abundance and the concentration of methylated As in paddy soil solutions also exhibit a strong positive correlation [29]. The amount and form of OM in wetlands is also key, for example, several experiments carried out in microcosms using paddy soils have demonstrated that the amendment of OM promotes the activity of As^{III} oxidizing bacteria [28]. The application of rice straw can increase the community diversity of As^{III} oxidizing bacteria [60], and the activity of

As^{III} methylation microbes in paddy soils [28, 29]. Straw also has an impact on As^{V} detoxification reducing microbes, acting to moderately simulate their activity, but greatly enhance the total abundance of As^{V} reducers [28].

The concentration of SO_4^{2-} in paddy soils strongly influences microbial community compositions, modifying both As^{III} oxidation and As^{V} detoxification reduction activity. It is postulated that this is due to the possible sharing of microbial groups of sulfur oxidation and As redox [61]. The microbial community composition of bacteria/archaea involved in As biotransformations is also particularly sensitive to iron concentrations. This is reasonable, especially considering that the absorption-desorption dynamics of iron /oxyhydroxides and As^{V} influence the concentration and species of bioavailable As in wetlands [41, 42]. For the microbial communities carrying out As^{III} methylation, it is the available NO_3^--N, NH_4^+-N, that appears to be the most sensitive environmental parameter influencing community composition [61]. Other factors, such as pH, redox potential, alkalinity, temperature and dissolved oxygen, also contribute and influence As biotransformation microbial abundance and activity [46]. However, investigation into this topic is still in its infancy. Much remains to be done to improve our understanding of how we can optimize the function of microbial mediated As biotransformations by changing the management of local wetland environments. A significant hurdle, blocking this goal has been the lack of suitable methods to observe and measure the dynamic environmental conditions, at scales appropriate to the biota driving the change. However, with the development of new multi-parameter, visualization tools such as diffusive gradients in thin films (DGT)/planar optode sandwich sensors [84, 85] and advanced radiography and isotope imaging, *in situ* mapping of As and other key elements is now possible. Employing these technologies concurrently with 2D enzyme activity plots (zymography) and microbial imaging, i.e. fluorescence *in situ* hybridization (FISH) or oligonucleotides labeled probes with light emitting chromophores [86], offers further exciting possibilities to unravel the complex environment-biota interactions impacting on wetland As release.

4 Concluding remarks and perspectives

Microbes act as the ‘switch’ turning a wetland from an As sink to source through As^{V} reduction, As^{III} oxidation, As^{III} methylation, and As volatilization processes (Figure 1). As^{V} reducing bacteria/archea can enhance As mobilization from sediments to water [54, 75], while As^{III} oxidizing microbes act to decrease As mobility and bioavailability [3]. The two groups of As^{V} reducers and As^{III} oxidizers act in tandem, controlling the direction/path of the inorganic As cycle. While wetland As^{III} methylaters create organic As species ($MMAs^{V}$, $DMAs^{V}$, $TMAs^{III}$), they also generate volatile As, promoting its release into the atmosphere [2].

Considering the key role wetlands play in delivering essential ecosystems services and the large area they occupy, the microbial mediated As biotransformations they host/support remain indispensable components of a ‘safe’ global As biogeochemical cycle, one that functions in the best interests of humankind. Failure to live in balance with As’ complex biogeochemistry can have devastating consequences, from the release of As from near-surface wetland sediments to underground drinking water supplies [72], to its transfer into rice plants [41].

Better management of wetland resources for optimized microbial control of As could potentially yield huge gains in public and environmental health. However more research is needed to improve our understanding of how to make best use of these microbial mediated reactions. We recommend research attention is immediately directed at gaps in our understanding of wetland As cycling, such as microbial organic-As degradation, as the literature available on this topic is scant. Furthermore, continued improvements to the technologies available to study *in situ*, both the chemistry and biology of the mercurial wetland environment is needed.

Acknowledgements

The authors declare no conflicts of interest and financial disclosures. We would like to thank the Chinese Academy of Sciences President's International Fellowship Initiative (CAS-PIFI 2016VEC001) and China Postdoctoral Science Foundation (No. 212400241).

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Table 1. Structure of prevalent As species in the environment.

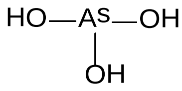
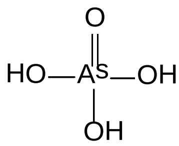
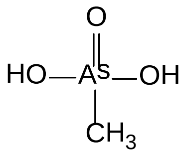
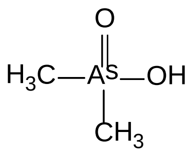
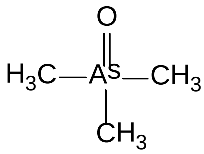
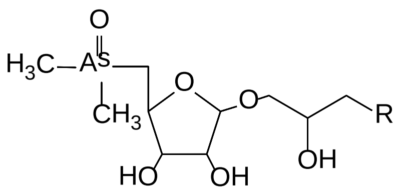
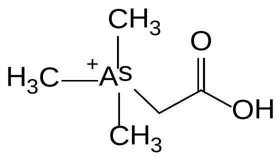
Species	Structure of As speciation
Arsenite, As^{III}	
Aesenate, As^{V}	
Methylarsonate, $MMAs^{V}$	
Dimethylarsinate, $DMAs^{V}$	
Thrimethylarsine oxide, TMAO	
Aesenosugars	
Arsenobetaine, AsB	

Table 2. The quality guidelines for As contamination in wetlands from different countries.

Sediment quality guidelines in various countries	Countries	Level	Arsenic concentration (mg kg^{-1})	References
Hongkong ISQVs	China	ISQV-low	8.2	[87]
		ISQV-high	70	
Sediment Quality Criteria	China	Class I	20	[16]
		Class II	65	
Canadian Environmental Quality Guideline	Canada	ISQGs	7.24	[15]
		PEL	41.6	

ISQV, interim sediment quality value; ISQGs, interim sediment quality guidelines; PEL: probable effect level.

Table 3. Summary of recently detected arsenic contaminated wetlands.

Wetland types	Country	Sampling Location	As concentration (mg kg^{-1}/ μg L^{-1})	References
Coastal wetlands	China	Yellow River delta	38	[32]
			45	
		Yangtze River delta	10	[33]
Inland wetlands	U.S.	Massachusetts	20-2100	[36]
	Spain	Guadalquivir	20	[38]
		Fatehpur	72-114	
Paddy soils	Bangladesh	Dhumrakandi	62-138	[26]
		Paranpur	73-77	
		Faridpur	34	
	India	De Ganga	17	
	China	Chenzhou	60	[61]

		Qiyang	79	
		Anqing	19	
		Jiaxing	20	
		Yingtan	16	
		Jingzhou	19	
		Changde	16	
		Jiangmen	25	
		Guilin	21	
		Guiyang	21	
		Zhanjiang	18	
Wetland waters	Bangladesh	Malahar	60	[23]
		Gerajan	80	
		Dohuria	11-14	

Behi	11
Porabait	26
Barakhaillah	20
Jora	11
Uhila	18
Barakuri	11
Jerukuri	11
Bigaira	11

Figure caption

Figure 1. Sources of As introduced to wetland, microbial mediated As biotransformation in wetland, and genes responsible for As^{V} respiratory reduction, As^{V} detoxification reduction, As^{III} oxidation, and As^{III} methylation.